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Review

Waste animal fats as feedstock for biodiesel production using non-catalytic supercritical alcohol transesterification: A perspective by the PRISMA methodology

Pedro Andreo-Martínez [a,b,*], Víctor Manuel Ortiz-Martínez [c,**], María José Salar-García [c], José Manuel Veiga-del-Baño [a], Antonio Chica [d], Joaquín Quesada-Medina [b]

[a] Department of Agricultural Chemistry, Faculty of Chemistry, University of Murcia, Campus of Espinardo, 30071 Murcia, Spain
[b] Department of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus of Espinardo, 30071 Murcia, Spain
[c] Department of Chemical and Environmental Engineering, Technical University of Cartagena, Campus Muralla del Mar, 30202, Cartagena, Spain
[d] Instituto de Tecnología Química, Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022, Valencia, Spain

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ABSTRACT

Global warming and fossil fuel depletion have boosted the search for alternative and renewable fuels with a low environmental impact. Biodiesel exhibits many advantages over conventional diesel including the possibility of being produced from renewable sources such as waste oils and fats. Specifically, waste animal fats are receiving increased attention as an alternative to vegetable oils for biodiesel production. This low-cost feedstock allows the mitigation of environmental pollution and can also improve biodiesel features by increasing cetane number and enhancing oxidative stability. Among the different technologies available for biodiesel production, supercritical processes offer important advantages over conventional catalytic transesterification in terms of process efficiency and reaction time. According to the increasing interest and number of research articles published in this field in the last years, this work focuses on the systematic review of the technology by using the Systematic Reviews and Meta-Analysis (PRISMA) methodology. This work describes the state of the art of non-catalytic supercritical production of biodiesel using animal fats as a feedstock and discusses the key aspects of the process such as the type of fat used, operation variables including reaction time, temperature, solvent excess, pressure, and solvent excess, and the final properties of the synthesized biodiesel.

Contents

* Correspondence to: P. Andreo-Martínez, Department of Agricultural Chemistry, Faculty of Chemistry, University of Murcia, Campus of Espinardo, 30071 Murcia, Spain.
** Corresponding author.
E-mail addresses: pam11@um.es (P. Andreo-Martínez), victor.ortiz@upct.es (V.M. Ortiz-Martínez).

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Introduction

Fossil fuels remain the main source of primary energy accounting for over 80 % of worldwide energy consumption. The continuous consumption of non-renewable resources is leading to their fast depletion while causing the accumulation of CO_2 and other greenhouse gases (GHGs) in the atmosphere (Osman et al., 2021). Also, energy demands are expected to rise by over 25 % by 2040, which claims for a shift toward the use of renewable and carbon-neutral fuels to ensure environmental and economic sustainability (Dassey et al., 2014; IEA, 2017; König et al., 2020). Biofuels from waste still provide 10 % of the total energy production, however, they are called to play a key role in energy supply and, more importantly, will contribute to a reduction in GHG emissions (Jahromi et al., 2021; Oh et al., 2018; Prabakaran et al., 2022).

The interest in biodiesel as a sustainable source of energy continues to increase due to its advantages over fossil fuels (Deshmukh et al., 2019; Fazal et al., 2019; Jayakumar et al., 2021; Li et al., 2019; Naveenkumar & Baskar, 2021; Srivastava et al., 2020). In terms of chemical composition, biodiesel typically consists of a blend of fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs) with virtually sulfur-free content (Adewale et al., 2015; Hoekman et al., 2012; Quayson et al., 2020). Compared to conventional diesel, biodiesel exhibits a superior flashpoint, higher cetane number, and its combustion produces lower carbon monoxide emissions and decreased levels of nitrated compounds, less particulate matter, and lower emissions of both unburned hydrocarbons (UHC), and aromatic hydrocarbons (Kaya et al., 2018). Moreover, biodiesel offers safer handling and non-toxicity. This translates into a lower harmful impact on human health versus the exhaust produced from conventional diesel due to lower amounts of carcinogenic compounds. Furthermore, biodiesel has almost the same energy efficiency as petroleum diesel with additional lubricity benefits for engine performance (Ayetor et al., 2015; Dahiya et al., 2018; Giakoumis & Sarakatsanis, 2019; Liu et al., 2019).

The transesterification reaction is the most commercially used method for biodiesel synthesis. Transesterification implies the conversion of triglycerides (TG) and/or free fatty acids (FFAs) into esters using an organic solvent, generally short-chain alcohols (see Fig. 1). The sources for these lipids include both edible and non-edible oils, discarded and recycled greases, animal fats, and edible oil wastes, presenting different fatty acid composition profiles (Ait Belale et al., 2021; Ishak & Kamari, 2019; Rezania et al., 2021; Sharma et al., 2021; Singh et al., 2020).

Methanol or ethanol are usually used as alcohol reactants to produce biodiesel from vegetable oils and animal fats (Verma & Sharma, 2016). Methanol is more frequently used in comparison to ethanol because of its availability and lower cost. Other short-chain alcohols such as isopropanol can be employed as an alternative (Huang et al., 2015; Redel-Macías et al., 2021). The transesterification reaction is influenced by several variables which include reaction temperature, reaction time, alcohol-to-oil ratio, type and amount of catalyst, and feedstock composition (Banerjee et al., 2018; Vinoth Arul Raj et al., 2021). This process can be performed in the presence of acid and alkali catalysts at mild conditions or, alternatively, using free-catalyst supercritical conditions. The first two methods are limited by the feedstock composition in terms of free fatty acids (FFA) and water content. The presence of these compounds in the raw material can cause saponification during biodiesel production reducing the reaction yield and promoting catalyst deactivation (Folayan et al., 2019; Hayyan et al., 2021). Comparatively, free-catalyst processes using supercritical conditions enable the simplification of posttreatment and purification steps. Supercritical technology generally implies the use of high pressure and temperature conditions beyond the critical point of the alcohol used (e.g., 8.01 MPa and 512.6 K for methanol) (Akkarawatkhoosith et al., 2019; Farobie & Matsumura, 2017b). This technology offers unique advantages for the reaction by creating a homogeneous media which enhances the mixing of reactants as well as heat and mass transfer, improving production yields and greatly shortening reaction time. Moreover, supercritical conditions facilitate scalability and continuous operation (Aboelazayem et al., 2021; Andreo-Martínez et al., 2020; Farobie & Matsumura, 2017a; Feng et al., 2022).

The valorization of waste animal fats into biodiesel has become an interesting option (Adewale et al., 2015; Encinar et al., 2011;

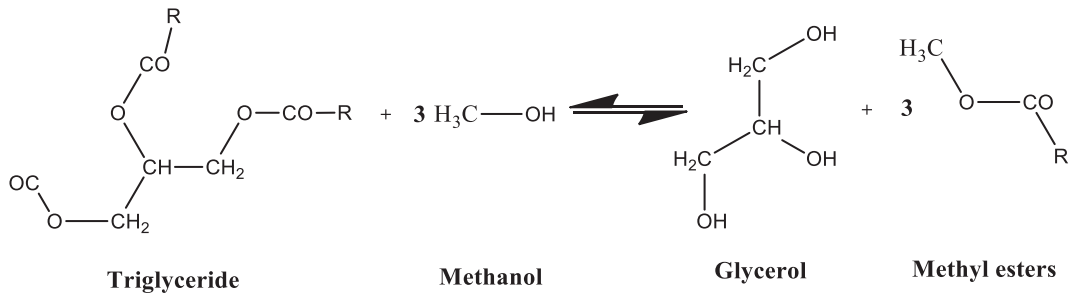

Fig. 1. Transesterification of triglycerides (TG) in methanol.

Marwaha et al., 2018; Vinoth Arul Raj et al., 2021). Waste animal fats are an attractive feedstock since their cost is substantially lower in comparison to vegetable oils (Banković-Ilić et al., 2014a; Habib et al., 2020, 2021; Jayakumar et al., 2021; Simsek & Uslu, 2020). The utilization of animal fats avoids the necessity for waste disposal while contributing to the supply of biofuels. This is partly explained by the fact that the market for animal fat is significantly more limited in comparison to the vegetable oil market because much of the animal fat produced, for example in the U.S., is considered non-edible by humans. Waste animal fats obtained from meat processing industries, tanneries, and slaughterhouses are seemed like suitable feedstock for biofuel synthesis due to their renewable nature, good calorific value, chemical inertness, and zero corrosivity. The main sources of animal fats are beef, tallow, poultry, and lard fats. As a representative case, the U.S. generates >1.4 billion gallons of animal fat and waste cooking oil per year, and over 74 % of the non-edible grease and tallow are used for animal feeding and to produce chemicals such as soaps and lubricants (Feddern, 2011).

Due to the increasing interest in animal fats as biodiesel feedstock, this work offers a systematic review in the field using the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) methodology (Ortiz-Martínez et al., 2019). The PRISMA methodology offers a systematic approach for identifying, selecting, and critically appraising relevant primary research to synthesize reported scientific information, strengthening the validity of the conclusions of separate studies, and highlighting the uncertainty areas in which further research is necessary. This methodology has been scarcely applied in engineering fields; however, its use can be of great help for the systematic review of the research literature. Thus, this work discusses the current state of the art of biodiesel production from animal fats in supercritical alcohol under the PRISMA methodology.

Method

This systematic review was designed in accordance with the PRISMA guidelines. The methodology describes how data from available studies need to be collected and analyzed by establishing explicit and reproducible methods that identify, choose, and critically assess relevant research. The PRISMA Statement includes 27 items in the form of a checklist and a flow chart of four main phases that help users to prepare reviews and meta-analyses. These 27 items are listed for the main categories of i) title, ii) abstract, iii) introduction, vi) methods, v) results, vi) discussion, vii) conclusion, and viii) funding, being used to reduce possible bias in any final evaluation of the results (Page et al., 2021).

Protocol and registration

The protocol followed for this systematic review has been registered in neither Systematic Review nor Meta-analysis databases.

Eligibility and exclusion criteria

All studies, internationally, were considered. The eligibility criteria for the preparation of this systematic review were as follows. Inclusion criteria: i) original primary articles on catalyst-free biodiesel production in supercritical conditions using animal fat as raw material because they are the core of scientific research (Alkhawtani et al., 2020), ii) articles issued from inception to February 21st 2021; Exclusion criteria: i) non-systematic review articles; ii) manuscripts in a language different from English, iii) essays and conference proceedings, iv) book chapters or complete books, v) editorial matter, vi) works on biodiesel production when employing different techniques and feedstocks from that stated in the inclusion criteria and that focus on co-solvent role and catalyst materials as main study subjects.

Information sources and search strategy

The research databases Scopus, Web of Science, Science Database, and PubMed were searched on 21 February 2021. The search identified works published from inception to 21 February 2021 inclusive. The following search criteria were entered into the four databases: '(biodiesel* OR FAME*) AND (supercritical*) AND (fat* OR tallow OR pork OR beef OR poultry OR chicken OR duck OR suet OR lard)'. No language restriction was applied. In the case of the Scopus database, search options were 'title, abstract, and keywords'. Web of Science search option was 'theme' for all databases. The Science Database option search was 'all fields except full text (NOFT)' and 'all fields' for PubMed.

Study selection

After the database search stage, a three-step procedure was followed in order to review all found records under the established eligibility criteria: firstly, by reading the title, secondly by reading the abstract, and finally by reading the complete work. The articles found on the four databases were screened with the software 'EndNote-X9' with the aim of identifying duplicates and classifying the works considering inclusion/exclusion criteria. Two of the authors (P.A.-M and V.M.-O) were part of the 'review team' to provide measures with the objective of minimizing bias and possible random errors at all review stages, independently revising titles, abstracts, and full texts of the articles for potential selection.

Data extraction and data items

The extraction of quantitative and qualitative data from articles was carried out by following a data extraction form designed by the authors in previous work (Ortiz-Martínez et al., 2019). The data items included for data extraction were animal fat type, molecular weight, free fatty acid, water content, process type, solvent type, fat-solvent ratio, temperature, pressure, reaction time, and FAME yield if available. Table 1 displays a portion of the extracted data.

Risk of bias in individual studies

Bias is deemed as a systematic error that can cause the underestimation or overestimation of the true effect (Higgins et al., 2019). The risk of bias was assessed according to The Methods Guide for Comparative Effectiveness Reviews (Viswanathan et al., 2008). The form used for bias evaluation is presented in Table 2. Each risk of bias question can score 0 ('unclear/not reported'), 1 ('partially reported'), and 2 ('fully reported').

Item 1 (Clear stated aim) was scored with 0 if the aim of the manuscript did not clearly correspond to the research, scored with 1 if the aim of the manuscript was confusing or ambiguous, and scored with 2 if the aim of the manuscript was clearly reported. Item 2 (Accurate experimental design) was scored with 0 if the experimental design was not reported, scored with 1 if the experimental design was not clearly reported, and scored with 2 if the experimental design was accurately reported. Item 3 (Identification and evaluation of sample) was scored with 0 if no animal fat properties were reported, scored with 1 if some animal fat properties such as density, water content, or FFA content were reported, and scored with 2 if, in addition to the aforementioned properties, the fatty acid profile of the animal fat used was reported. Item 4 (Comparability or reproducibility) was scored with 0 if the experimental work required the use of some overly sophisticated or specific instrumental apparatus, scored with 1 if not very sophisticated laboratory equipment but with low reproducibility in measurements was used, and scored with 2 if experimental work can be easily reproduced in a chemical engineering laboratory. Item 5 (Other bias) was scored with 0 if the abstract, description of the method, and the conclusions were poorly described, scored with 1 if the abstract, the description of the method, and the conclusions were too brief, and scored

Table 1
Bibliographical results by the PRISMA methodology (summary) (MG: monoglycerides, DG: diglycerides, TG: Triglycerides).

Ref.	Feedstock	Molecular weight ($g \cdot mol^{-1}$)	FAA (%)	Water (%)	Process type	Solvent	Fat to solvent ratio	T (°C)	Pressure (MPa)	Time (min)	FAME or FAEE yield (%) (or TG conversion as indicated)	Reported biodiesel properties
(Marulanda et al., 2010b)	Chicken fat	867	4	–	Batch	MeOH	1:6	400	41.1	6	88.0	Pour point: <0 °C; viscosity at 40 °C: 1.46 times higher than for diesel fuel #2 and virtually the same as for commercial biodiesel. Free glycerol: 0.014 wt%; total glycerol: 0.049 wt%. MG: 0.083 wt%; DG: 0.065 %; TG: 0.016 wt%.
(Marulanda et al., 2010a)	Chicken fat	867	–	–	Continuous flow	MeOH	1:9	375	20	10	84.0	Free glycerol: 0.004 wt%; total glycerol: 0.012 wt%. MG: 0.022 wt%; DG: 0.011 %; TG: 0.0 wt%.
(Manuale et al., 2011)	Chicken oil	–	23.6	0.12	Continuous flow	MeOH	1:20	280	11	60	˷93.0	Free glycerol: 0.02 wt%; total glycerol: 0.14 wt%.
(Anitescu & Bruno, 2012)	Chicken fat	–		–	Batch	MeOH	1:9	400	10	5–9	–	Cetane number: 59–61 (cetane number of commercial biodiesel: 53–57)
(Shin et al., 2012)	Refined lard	–	0.08	No detected	Batch	MeOH	1:45	335	20	15	89.1	Acid value (mg KOH/g): No detected
(Ong et al., 2013)	Leather tanning waste	–	14.9	–	Batch	MeOH	1:40	325	12	10	1.05 (mol/l)	–
(Marulanda-Buitrago & Marulanda-Cardona, 2015)	Beef tallow	–		–	Batch	EtOH	1:15	400	24–27	40	98	Humidity: 3.5 %
(Manuale et al., 2015)	Chicken oil	–	24.0	0.12	Continuous flow	MeOH	1:20	280	11	60	97.0	Density at 15°: 0.876 g/m^3; viscosity at 40 °C: 5.7 mm^2/s; flash point: 163 °C; sulfated ash: 0.015 wt%; water content: 800 mg/kg; free glycerol: 0.019 wt%; total glycerol: 0.17 wt%
(Shah et al., 2015)	Pig fat	–	–	–	Batch	MeOH	1:67.5	290	–	–	99 (TG conversion)	–
						EtOH	1:47		–	–	99 (TG conversion)	–
(Poudel et al., 2017)	Pig fat	–	–	–	Batch	MeOH	1:67.5	290	11.4–18.7	60	99 (TG conversion)	Total glycerol: 8.48 wt%
						EtOH	1:47		9.8–14.5	60	99 (TG conversion)	total glycerol: 0.00 wt%
(Bolonio et al., 2018)	Tallow	856.4	10.4	0.31	Batch	EtOH	1:40	350	11.5–20	40	98.4	–
(Yuliana et al., 2020)	Leather tanning waste	–	15.24	12.37	Batch	EtOH	1:40	374.6	15 MPa	47.4	98.9	Density at 15 °C: 0.857 g/cm^3; viscosity at 40 °C: 2.36 mm^2/s; Flash point: 98.4 °C; cetane number: 51.2; cloud point: 9.8 °C; acid value: 0.31 mgKOH/g

Table 2
Summary of bias scoring for selected articles.

Item	(Bolonio et al., 2018)	(Anitescu & Bruno, 2012)	(Manuale et al., 2011)	(Manuale et al., 2015)	(Marulanda et al., 2010a)	(Marulanda et al., 2010b)	(Marulanda-Buitrago & Marulanda-Cardona, 2015)	(Ong et al., 2013)	(Shah et al., 2015)	(Shin et al., 2012)	(Poudel et al., 2017)	(Yuliana et al., 2020)
1. Clear stated aim	2	2	2	2	2	2	2	2	2	2	2	2
2. Accurate experimental design	2	2	2	2	2	2	2	2	2	2	2	2
3. Identification and evaluation of sample	1	1	1	1	2	2	1	1	2	2	2	2
4. Comparability or reproducibility	2	2	2	2	2	2	2	2	2	2	2	2
5. Other bias (Method description, conclusions…)	2	2	2	2	2	2	2	2	2	2	2	2
6. Adequate statistical analyses	0	0	0	0	0	0	0	0	0	0	0	2
Total	9	9	9	9	10	10	9	9	10	10	10	12
The overall risk of bias	M	M	M	M	L	L	M	M	L	L	L	L

Item score: 0 = Not reported/unclear, 1 = not adequately assessed, 2 = adequately assessed.
Total score: M = Moderate (7–9); L = Low (10−12); H = High (6–0).

with 2 if the abstract, the description of the method and the conclusions were correctly described. Item 6 (Adequate statistical analyses) was scored with 0 if no statistical analysis was reported, scored with 1 if some statistical analysis such as surface response or similar was performed, and scored with 2 if means and standard deviation of FAMEs yield values were reported.

Total scores range from 0 to 12 for each bias question. A score within the range of 0–6 implies high-risk bias, the range 7–9 implies moderate-risk bias, and the range 10–12 was considered as low-risk bias. Bias evaluation was carried out by the reviewer team.

Synthesis of results and statistical analysis

Collected data and results in the studies were also checked independently by the reviewer team to find differences in the extracted data if any. No meta-analysis was performed since the set of articles included in this review lack sufficient statistics such as sample mean and standard deviation of FAME or FAEE yield to pool studies in an aggregate data meta-analysis (Cook et al., 1997).

Results

Search results

The flow-chart protocol for article selection is displayed in Fig. 2. The electronic database Scopus returned 179 works, Web of Science returned 464 works, Science Database returned 17 works and PubMed returned 19 works. The 679 works provided were crossed with the software 'EndNote-X9' for duplicate screening. One hundred and twenty works were eliminated in this stage. After revising the abstracts of the remaining articles individually, the works directly linked to the study subject were selected (330) and the full texts were obtained from different web pages. Two articles were wrongly indexed as conference papers in the Scopus database and were finally included in the selected articles of the present systematic review (Anitescu & Bruno, 2012; Marulanda et al., 2010a), and one work was eliminated due to it was a conference abstract (Babcock et al., 2008). One additional article was considered eligible among the bibliography set formed by the 330 pre-selected articles (Yuliana et al., 2020). On the other hand, several articles could be classified into two or more suppression groups, however, the reviewer team adopted the final criterion by agreement. Eventually, a total of 12 articles were considered eligible according to the assessment criteria of full-text eligibility.

Results of individual works and analysis of characteristics

The findings and characteristics for the 12 eligible works in the present systematic review are summarized in Table 1, including feedstock type, water, and FFA content, operation mode, solvent type, and reaction conditions such as temperature, pressure, and time reported for optimum performance and maximum FAME yield. Moreover, Table 1 displays the reported properties of the final product (biodiesel). Some of the selected articles lacked some relevant data (Anitescu & Bruno, 2012; Bolonio et al., 2018; Manuale et al., 2011; Marulanda-Buitrago & Marulanda-Cardona, 2015) and were requested to the authors by email. Chicken fat or oil was used as feedstock in 5 (41.66 %) articles, pig fat or refined lard was used as feedstock in 3 (25.00 %) articles, leather tanning waste in 2 (16.66 %) articles, and beef tallow and undefined tallow were used as feedstock in 1 (8.33 %) article. The 12 selected articles were published from 2010 to 2020. Attending to the address of corresponding authors, the affiliation corresponds to 7 countries: 3 were published in the USA, 3 in Korea, 2 in Argentina, 2 in Indonesia, 1 in Spain, and 1 in Colombia. The 12 works were published in eight different journals: 3 in the Journal of Supercritical Fluids, 3 in Energy and Fuel, 1 in Fuel, 1 in Energies, 1 in Fuel Processing Technology, 1 in CT&F-Ciencia, Tecnología y Futuro, 1 in Process Safety and Environmental Protection and 1 in Biomass and Bioenergy.

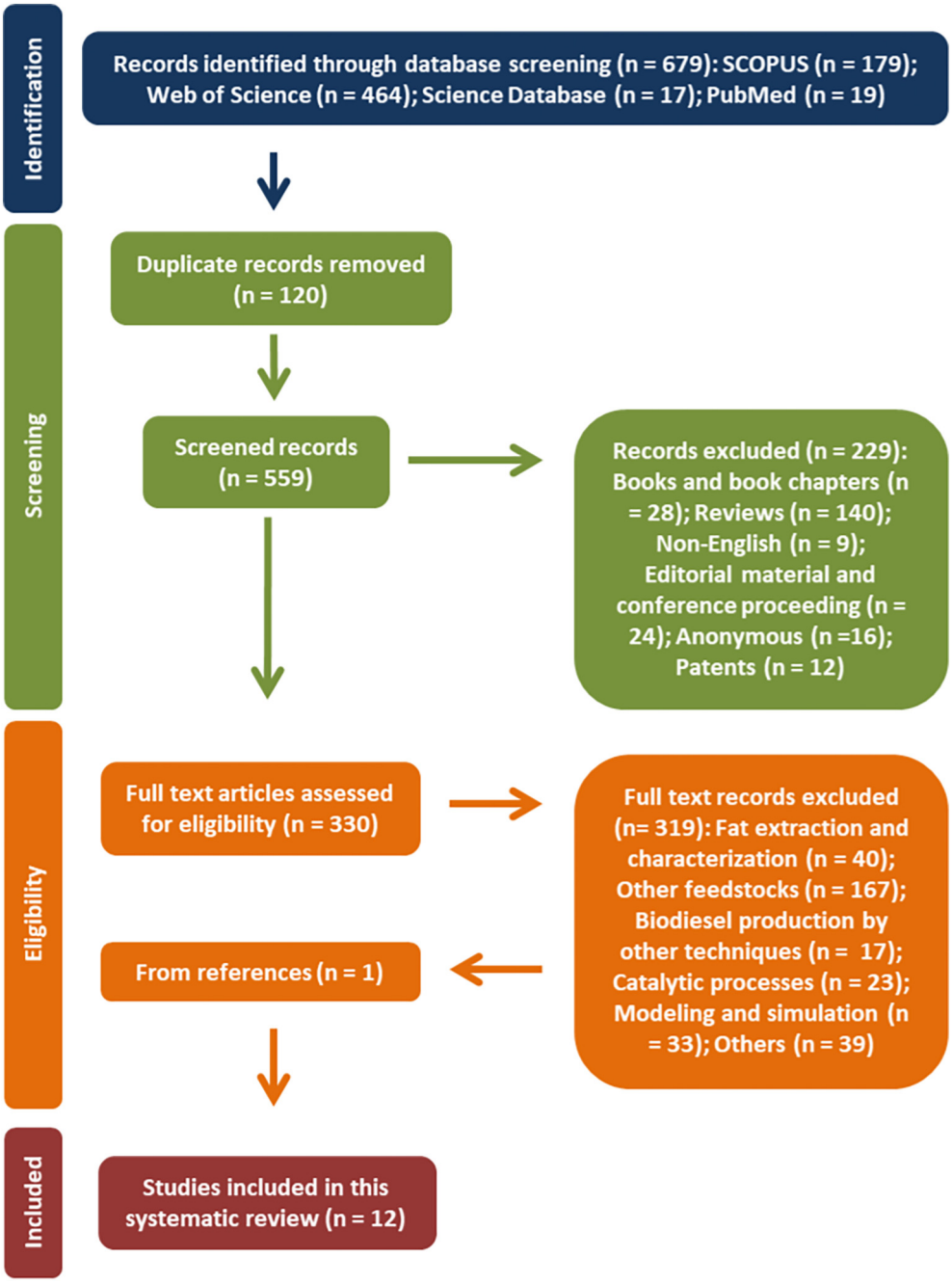

Fig. 2. Flowchart of systematic review according to the PRISMA method.

Risk of bias

According to the score classification provided in the Risk of bias in individual studies section, low-risk bias was obtained for 6 articles included in this systematic review, and moderate-risk bias was obtained for 6 articles. The articles presented some limitations in the identification and evaluation of samples, and a lack of statistical analyses. Table 2 displays the detailed scoring for the selected articles.

Limitations

By definition, the limitations of systematic reviews are posed by the research database employed, search terms used, and the established inclusion and exclusion criteria. For instance, the work by Yuliana et al. (Yuliana et al., 2020) was not found in any of the four comprehensive databases selected using the chosen Boolean stream. Nevertheless, the search procedure followed can be considered exhaustive and very few relevant studies can be expected to have not been selected. As commented, the English language was chosen as inclusion criteria, which can arise bias in the search (Ferreira González et al., 2011; Ortiz-Martínez et al., 2019). Finally, the absence of sufficient statistics in the articles selected made it impossible to perform a meta-analysis since none of the 12 selected articles reported mean values or standard deviation of variables such as the FAME or FAEE yields.

Discussion

In this section, the results obtained by the PRISMA method are grouped according to different key factors which affect not only the

Table 3
Fatty acid composition of animal fats (wt%). SFAs = saturated fatty acids, MUFAs = monounsaturated fatty acids (*including ricinoleic fatty acid), PUFAs = polyunsaturated fatty acids, UFAs = unsaturated fatty acids (*including ricinoleic fatty acid).

Reference	(Marulanda et al., 2010b)	(Marulanda et al., 2010a)	(Shin et al., 2012)	(Marulanda-Buitrago & Marulanda-Cardona, 2015)	(Rohman et al., 2012b)	(Anitescu & Bruno, 2012)	(Bolonio et al., 2018)	(Yuliana et al., 2020)
Animal fat	Chicken fat	Chicken fat	Refined lard	Beef tallow	Pig fat	Chicken fat	Tallow	Leather tanning waste
Myristic (C14:0)	–	–	1.8	3–6	1.3	–	3.2	3.01
Palmitic (C16:0)	21.0	21.0	24.7	24–32	20.66	21	27.3	26.83
Palmitoleic (16:1)	7.7	7.7	2.5	–	1.98	7.7	2.9	3.99
Margaric (C17:0)	–	–	0.2	–	0.48	–	1.2	0.42
Stearic (C18:0)	5.5	5.5	12.1	20–25	10.91	5.5	21.6	14.34
Oleic (C18:1)	48.5	48.5	44.4	37–43	39.12	48.5	38.5	43.32
Linoleic (C18:2)	17.3	17.3	11.9	–	19.56	17.3	3.1	5.95
Linolenic (C18:3)	Traces	Traces	1.5	–	1.21	Traces	0.2	2.03
Arachidic (C20:0)	–	–	–	–	0.15	–	0.1	0.11
Gadoleic (C20:1)	–	–	–	–	0.97	–	0.5	–
Behenic (C22:0)	–	–	–	–	0.03	–	–	–
Erucic (C22:1)	–	–	–	–	0.14	–	–	–
Nervonic (C24:1)	–	–	–	–	–	–	–	–
Others		–	0.9	–	–	–	–	–
SFAs	26.5	26.5	–	45.6	–	26.5	–	–
MUFAs	–	–	–	–	–	–	–	–
PUFA	–	–	–	–	–	–	–	–
UFA	73.5	73.5	–	–	–	73.5	–	–

biodiesel yield but also its final properties. Among these parameters, the most relevant are reaction time and temperature, followed by pressure (at values lower than 20 MPa) and the type of solvent. Finally, the nature of the animal fats and therefore the FFA and water content are other parameters to be into consideration in the process. According to this, such factors have been grouped in different sections in which their effects on biodiesel yield and properties are discussed.

Nature of animal fats as biodiesel feedstock

The use of animal fats as biodiesel feedstock in conventional catalytic processes is hindered by the high content of FFA and water compared to vegetable oils. The presence of these compounds increases the processing costs due to the need for additional pre-treatment stages. Otherwise, the process yield would be reduced by the reaction of such impurities with the catalyst to produce soaps, which in turn makes harder the separation of biodiesel from glycerol (Bouaid et al., 2016; Hayyan et al., 2021). Thus, alternative methods such as non-catalytic synthesis in supercritical alcohol have been proposed for biodiesel production from animal fats (Mathew et al., 2021). Despite these limitations, the use of animal fats as an alternative feedstock to refined vegetable oils brings multiple benefits such as low cost. A broad variety of animal fats have been researched for biodiesel production, e.g., chicken fat, chicken oil, refined lard, leather tanning waste, beef tallow, or pig fat, among others (see Table 3). Marulanda et al. (Marulanda et al., 2010a, 2010b) studied the use of chicken fat with different FFAs content to produce biodiesel via transesterification under supercritical conditions. Their results show that chicken fat with a low amount of FFAs (4 wt%) is suitable to produce biodiesel without glycerol generation by using a low excess of methanol. Among the different conditions studied, it has been reported that the maximum FAME yield achieved was 88 % at 400 °C and 41.1 MPa, 6 min of residence time, and a methanol to oil fat molar ratio of 6:1 in a batch mode process (Marulanda et al., 2010b). Under these conditions, most of the glycerol produced was either thermally decomposed and/or reacted with the alcohol excess, whereas a small amount of methanol/glycerol remained along with the biodiesel obtained whose purity matches the standards required. The same authors also analyzed the influence of the operational conditions on biodiesel production from chicken fat via supercritical transesterification with methanol in continuous mode (Marulanda et al., 2010a). Among the different conditions investigated, the best result in terms of TG conversion and glycerol decomposition was achieved at 375 °C, 20 MPa, with a methanol to chicken fat molar ratio of 9:1 and after 10 min of reaction time. One of the most important findings of this work is that the decomposition of the main FAMEs results in shorter methyl esters, which enhances the viscosity or cold flow of the biodiesel obtained.

Chicken-derived wastes have also been used by Manuale et al. (Manuale et al., 2011, 2015) to produce biodiesel under supercritical conditions. Chicken oil with a high FFA content of 23.6 % was used as feedstock and the performance of the process was compared to the performance of vegetable oils like soy and waste cooking oils, whose FFAs content is significantly lower (Manuale et al., 2011). The evolution of the FFAs in the biodiesel during the process over time decreased dramatically in the case of chicken oil, which might be mainly caused by the esterification and thermal decomposition. When monitoring the evolution of FFA content, it was observed that the feedstock with the least initial amount of FFAs increased its FFA content due to the hydrolysis of glycerides followed by a reduction caused by decomposition or esterification reactions. Regardless of the initial FFA amount, the content was lower than 1 % after 80 min of reaction time with a methanol to oil fat ratio of 20:1. Nevertheless, this percentage is higher than that established by the ASTM-6751 (ASTM D6751 - 20a Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, n.d.) and the EN-14214 (European Committee for Standardization, 2003) standards. An increase in the reaction time might help to reduce this parameter in order to match the standard. Regarding the water content, the results show a maximum of this parameter at 30 min of reaction time for all feedstocks employed and a very similar value at the end of the process regardless of the type of feedstock. These results demonstrate that the changes in water content during the process exclusively depend on the reaction time and not on the initial water content. A deeper analysis of these results shows that the thermolysis of glycerol generates water coupled to the formation of volatile compounds such as carbon dioxide. According to the evolution of the water content in the biodiesel produced over time, all feedstocks meet the ASTM-6751 (ASTM D6751 - 20a Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, n.d.) and the EN-14214 (European Committee for Standardization, 2003) standards after 60 min of reaction time (<0.05 %). Regarding the methyl ester content, a volcano pattern is shown for the three feedstocks evaluated. However, only the chicken oil allows reaching a percentage of methyl ester above the reference value fixed by the EN-14214 standard after 60 min of reaction time at 280 °C and using a methanol to oil ratio of 20:1. These findings prove the suitability of transforming chicken oil into biodiesel via free-catalyst transesterification in supercritical conditions,

encouraging the design of integrated processes to continuously produce biodiesel from this low-cost feedstock (Manuale et al., 2015).

Due to the numerous benefits of using animal-derived wastes as feedstock to produce biodiesel, Anitescu and Bruno (Anitescu & Bruno, 2012) used the advanced distillation curve method to analyze the volatility of the product synthesized through the supercritical transesterification of chicken fat and soybean oil and compared these values with the volatility of two commercial biodiesel samples. The properties of the biodiesel obtained from both renewable feedstocks exhibited better results than the commercial samples in terms of volatility and cetane numbers, which could promote the design of more efficient diesel engines. Specifically, the cetane number of chicken fat biodiesel fuel was in the range 59–61, while the cetane number of commercial biodiesel fuel was within the range 53–56.

In addition to chicken fat and chicken oil, pig-derived wastes have also been reported as a suitable option for biodiesel production. In 2012, Shin et al. (Shin et al., 2012) investigated the transesterification of refined lard in supercritical methanol and compared it with the use of waste lard from different restaurants. The composition of fatty acids in all samples was very similar, however, it is worth noting that the cooking of pork displayed higher FFA and water content. The results show that this fact does not affect the FAME content in the biodiesel obtained from waste lard since all waste lard samples provided similar FAME content to that provided by refined lard at the optimal reaction conditions. These results confirm that the transesterification of TG and the esterification of FFAs occur simultaneously during the process. These findings point to waste lard as a potential alternative to refined vegetable oil for biodiesel production in supercritical conditions, significantly reducing the cost of the overall process.

Since then, waste pig fat has been used more often for biodiesel production via supercritical methanol. For instance, in 2015 Shah et al. (Shah et al., 2015) used a non-isothermal method to analyze the transesterification kinetics of waste pig fat via supercritical alcohol. Their results show a positive impact of temperature on the conversion rate of fatty acids both in methanol and ethanol, being this parameter maximum in the case of using methanol. It was also found a lower value of apparent activation energy when using supercritical ethanol instead of methanol. The kinetic method proposed by Shah et al. (Shah et al., 2015) allowed them to obtain reliable kinetic parameters to produce biodiesel from waste pig fat via supercritical alcohols, reporting theoretical values very similar to the experimental results. A few years later, Poudel et al. (Poudel et al., 2017) compared the performance provided by different alcohols as solvents via supercritical transesterification of waste pig fat. The content of unsaturated fatty acids in lard is significantly higher than in other animal fats such as beef or chicken, being palmitic, stearic, oleic, and linoleic the predominant acids (see Table 3). Regarding the triacylglycerols composition, palmitooleoolein, palmitooleostearin and palmitoolepalmitin were predominant in lard, whose composition was very similar to chicken fat (Rohman et al., 2012a). Among the different operating conditions investigated by Poudel et al. (Poudel et al., 2017) to transform waste pig fat into biodiesel, their results clearly showed that the final yield is favored by temperature and reaction time, whereas an increase in the fat to alcohol ratio displayed no significant effect since an excess of alcohol might inhibit the transesterification of the lard. Although the results obtained by using ethanol and methanol, respectively, were very similar, the conversion reached using methanol was higher than that achieved using ethanol at a low reaction time. In both cases, after 60 min, the conversion of the transesterification reaction reached values above 99 %, for an alcohol to waste pig fat ratio of 1.5:1.

An alternative feedstock to produce biodiesel via supercritical transesterification is leather tanning waste, whose FFAs content is higher (14.9 %) in comparison with refined vegetable oils (usually lower than 1 %) (Ong et al., 2013). This fact makes difficult its transformation via an alkali-catalyzed process whereas the supercritical process allows up to 30 wt% of FFAs (Warabi et al., 2004). Ong et al. (Ong et al., 2013) studied the methanolysis of waste leather tanning to produce biodiesel under supercritical conditions. The process was investigated at 12 MPa using an alcohol to oil molar ratio of 40:1, temperatures from 250 to 325 °C, and reaction times from 2 to 10 min. The authors reported an increase in the conversion of TG and FFA to FAMEs with temperature, except for temperatures above 300 °C, from which thermal decomposition of the product is observed. Decomposition temperature depends on the type of methyl ester present in the final product (Quesada-Medina & Olivares-Carrillo, 2011). In this case, the degradation of the FAMEs generated from the leather tanning waste was analyzed by exposing the product obtained to supercritical conditions at 325 °C and 12 MPa for 2–30 min with methanol. The experimental procedure was the one described in (Alptekin et al., 2012). The thermal degradation of some FAMEs appears after 15 min of exposition time while in other cases it was undetectable up to 30 min, a much longer time than that investigated in such work (10 min). These results led authors to ignore the thermal degradation of FAMEs in the kinetic modeling of FAME formation, which incorporates reversible esterification and non-reversible transesterification. Leather tanning waste has also been recently used by Yuliana et al. (Yuliana et al., 2020) to obtain biodiesel by using a novel technique based on ethanol under supercritical conditions in a single-step process. The feedstock used for the process contains 15.24 % and 12.37 % of FFAs and water content, respectively. The authors combined response surface methodology with multilevel factorial design in order to optimize temperature, reaction time, and alcohol to oil ratio. According to their results, the maximum reaction efficiency in terms of FAEEs (99.68 %) was at 47.4 min of operating time under 374.6 °C and an ethanol molar ratio of 40.02. The predicted and experimental data only differed by 0.77 %, which verified the reliability of the model.

Along with chicken fat, pork lard, or leather tanning waste, other animal fats such as beef or mutton tallow have also been used to produce biodiesel. In 2015, Marulanda et al. (Marulanda-Buitrago & Marulanda-Cardona, 2015) reported the transformation of beef tallow, without any pre-treatment, into biodiesel via supercritical conditions. Batch mode was used to perform the experiments with ethanol to oil molar ratios from 9:1 to 15:1. The selected temperatures ranged from 350 °C to 400 °C and the reaction time was studied from 8 to 40 min. The beef tallow used in this work was solid at room temperature because of the high content of saturated fatty acids (45.6 %) compared with chicken fat whose content is much lower, around 32 %, being partially liquid (Banković-Ilić et al., 2014b). For this reason, the raw material needed to be melted before use. Among the different operating conditions investigated, the maximum conversion was obtained at 400 °C after 40 min of reaction time and using an ethanol to oil molar ratio of 15:1. Under these conditions, it was observed the thermal decomposition of short-chain ethyl esters and glycerol, which can potentially improve the properties of biofuel. More recently, in 2018, Bolonio et al. (Bolonio et al., 2018) analyzed the production of biodiesel from tallow in supercritical ethanol in a one-step process and compared the results with those obtained a two-step process. In this case, the tallow feedstock contains 20.8 % of FFAs and 314.6 ppm of water. Among the different reaction conditions evaluated, the highest percentage of FAEEs (98.4 %) was obtained with the one-step process at 350 °C and 40 min, with an alcohol to oil ratio of 40:1. Under these conditions, the percentage of FFAs in the final product was also the lowest (1.6 %). Although the maximum conversion was obtained with the one-step process, which is simpler and a suitable alternative for feedstock with low polyunsaturated compounds. On its part, the two-step method seemed to be suitable for feedstock with high content in unsaturated compounds.

All these research works encourage the use of different types of animal fats and wastes against refined vegetable oil to produce biodiesel via supercritical transesterification. The main advantage of this method over the conventional acid or basic-catalyzed process is that raw materials with high content in water and high FFAs such as animal-derived

waste can be successfully transformed into biodiesel avoiding the saponification of FFAs to form soap, which hinders the separation of the products obtained.

Operation mode

So far, most of the studies on biodiesel production from animal fats or wastes are commonly performed in batch mode due to the simplicity of the process. Thus, batch mode is usually used to optimize operational conditions as the first approach before shifting to continuous mode. For instance, Marulanda et al. (Marulanda et al., 2010b) optimized the transformation of chicken fat into biodiesel with supercritical methanol in batch mode reaching a maximum FAME yield of 88 %. Once the authors set the optimum conditions at 41.1 MPa, 400 °C, 6 min, and 6:1 methanol to oil molar ratio, they used the same feedstock to continuously feed the reactor. In this case, the optimal methanol to oil molar ratio was increased up to 9:1, and the reaction time up to 10 min, while the pressure was slightly decreased down to 20 MPa, and the temperature was set at 375 °C (Marulanda et al., 2010a).

The operation in batch mode is useful to determine the suitability of a specific feedstock to produce biodiesel via supercritical transesterification. For instance, as previously commented, Shin et al. (Shin et al., 2012) evaluated the suitability of different types of pig wastes (refined and raw lard) to produce biodiesel with supercritical methanol in batch mode. Marulanda-Buitrago and Marulanda-Cardona (Marulanda-Buitrago & Marulanda-Cardona, 2015) also chose batch conditions to evaluate the suitability of beef tallow to produce biodiesel with supercritical ethanol. By contrast, other authors preferred to start directly working in continuous mode due to their interest in the commercial application based on previous works using the same feedstock in batch mode. This is the case of Manuale et al. (Manuale et al., 2011) who used chicken fat along with other vegetable refined oils to produce biodiesel via supercritical methanol in continuous mode reaching a FAME yield of around 93 %. As their results showed the suitability of transforming chicken oil into biodiesel via supercritical methanol, a few years later the authors delved into the work and designed an energy integrated process to produce biodiesel using chicken oil, which allowed them to increase the FAME yield up to 97 % (Manuale et al., 2015).

Effect of solvent type

Supercritical transesterification is usually performed in short-chain alcohols such as ethanol and methanol as solvents. The amount of alcohol involved in the process is one of the key factors for maximizing reaction performance. Under supercritical conditions, the alcohol molecules react as free monomers due to the weakness of the hydrogen bonds. Despite the reactivity of the alcohol molecules under these conditions, an excess of alcohol is usually needed to reach a complete conversion of TG and accelerate the process, reducing the critical temperature of the overall process. However, it has been reported that the higher the amount of alcohol, the more complex the separation of biodiesel from the methanol phase. According to this, the alcohol to oil molar ratio is usually considered an optimization variable to balance the performance of the process and the energy consumed (Ortiz-Martínez et al., 2019).

The optimal alcohol to oil molar ratio depends on the nature of the feedstock and the type of alcohol employed. The minimum values were found for the transformation of chicken-derived fats in supercritical methanol. In batch mode, the lowest methanol to oil molar ratio was reported by Marulanda et al. (Marulanda et al., 2010b) and established at 6:1 to reach a FAME yield of 88 %. In continuous mode, a FAME yield of 84 % can be obtained using a molar ratio of 9:1 (Marulanda et al., 2010a).

Significantly higher alcohol to oil molar ratios have been reported when pork-derived wastes are used as feedstock, regardless of the type of alcohol used. When methanol is used as a solvent, the lowest alcohol to pig fat molar ratio was reported by Shin et al. (Shin et al., 2012). The authors found 45:1 as the optimum proportion between alcohol and fat, being able to reach a FAME yield of 89.1 % at 335 °C, 20 MPa, and 15 min in a batch mode process. However, higher methanol to pork fat molar ratio (67.5:1) allows the increase of FAME yield up to 99 % whereas the temperature was reduced by 290 °C (Poudel et al., 2017; Shah et al., 2015). Ethanol has also been used under supercritical conditions to transform pig fat into biodiesel. In this case, the ethanol to fat molar ratio which maximized the FAEE yield (99.9 %) was 47:1 at 290 °C in batch mode (Poudel et al., 2017; Shah et al., 2015).

Other animal-derived wastes such as leather tanning waste have also been used as feedstock in supercritical conditions as commented above. In this case, when methanol is used as a solvent, the optimum alcohol to oil molar ratio was found at 40:1 at a temperature of 325 °C in batch mode (Ong et al., 2013). A similar value was found by (Yuliana et al., 2020) when ethanol is used as the solvent instead of methanol (40.02:1). This molar ratio enabled a maximum FAEE yield of 98.91 %. Finally, the transesterification of tallow has been mainly performed with supercritical ethanol and in batch mode. The minimum ethanol to oil molar ratio (15:1) was reported by Marulanda-Buitrago and Marulanda-Carmona (Marulanda-Buitrago & Marulanda-Cardona, 2015), reaching the highest FAEE yield at 400 °C and 40 min of reaction time. By contrast, Bolonio et al. (Bolonio et al., 2018) found a significantly higher ethanol to oil molar ratio as the optimum for the process (40:1). In this case, the critical temperature decreased by 350 °C whereas the reaction time was 40 min with a resulting FAEE yield of 98.4 %.

Methanol and ethanol are the most frequent solvents employed in biodiesel synthesis. Among them, so far methanol is the most frequently used because FAME extraction from the reaction media is easier in comparison to the extraction of FAEEs. However, methanol is a non-renewable solvent and its replacement by ethanol has been gaining importance in the last few years in order to design a completely environmentally friendly process. Moreover, ethanol exhibits other benefits compared with methanol such as lower toxicity. However, as previously commented, regardless of the type of solvent selected, it is crucial to optimize the alcohol to oil molar ratio, not only to maximize the performance of the process in terms of reaction yield, but also to optimize the energy requirements, the amount of reactant, and other reaction parameters such as the critical temperature.

Temperature and reaction time effects

Supercritical fat transesterification is largely affected by temperature and reaction time. In addition, these two parameters are crucial in determining process efficiency in terms of productivity and economy. The transesterification of animal fat under supercritical conditions needs significantly shorter times when compared to ambient and low-temperature conditions. Reaction time and temperature can be optimized separately or simultaneously to study their interaction. Among them, the temperature is usually considered the most relevant factor for non-catalyzed transesterification reactions (Bolonio et al., 2018). Although higher temperatures and longer reaction times generally lead to higher conversion rates, it is important to balance these two variables since the components of biodiesel formed in the reaction can be subjected to degradation and thermal decomposition (Quesada-Medina & Olivares-Carrillo, 2011; Salar-García et al., 2016).

Several works have shown that temperatures near or above 300 °C are beneficial for biodiesel production from animal fats. In this sense, Bolonio et al. (Bolonio et al., 2018) reported that the FAEE yield decreased by over 20 % when the reaction temperature was decreased from 350 to 300 °C using tallow as feedstock. For long reaction times, the final FAEE yield is limited by the degradation of mono- and polyunsaturated ethyl esters such as C18:1 and C18:2 ethyl esters. C18:2 degradation is more noticeable, accounting for 38 % after 120 min, while for C18:1 the degradation rate was over 4 %. C18:2 degradation can be

reduced by 22 % using a reaction time of 40 min. These results indicate that feedstocks with low percentages of polyunsaturated fatty acids are preferable for biodiesel production through single-step supercritical methods since they are more susceptible to thermal decomposition.

Higher temperatures than 350 °C can be used to obtain significant FAME yields in short reaction times. Marulanda et al. (Marulanda et al., 2010a) analyzed the continuous production of biodiesel using chicken fat as feedstock fat at temperatures within the range 300–400 °C obtaining optimal conditions at 375 °C (200 MPa) and only 9 min for a final yield of 84 %. In this case, and due to the severe temperature employed, decomposition of unsaturated FAMEs was also observed. Specific mechanisms such as denaturalization, oxidation, and trans-isomerization with subsequent decomposition were suggested as degradation processes that limited final FAME yield. These authors (Marulanda et al., 2010b) also studied the process in a batch reactor achieving a FAME yield of 88 % at 400 °C for 6 min. The FAME yield was improved using higher temperature and shorter reaction time in comparison to the previously mentioned work but in discontinuous mode.

Marulanda-Buitrago and Marulanda-Cardona (Marulanda-Buitrago & Marulanda-Cardona, 2015) analyzed the production of biodiesel from beef tallow studying the decomposition of FAEEs at 400 °C for 40 min reaction time. The ethyl ester C18:1 was found to fully decompose into cis-trans isomers and ethyl octadecanoate C18:0 via double bond hydrogenation reactions. Also, the decomposition of glycerol decomposition reactions was confirmed by the detection of water and glycerol ethers in the final product. Moreover, the appearance of short-chain ethyl esters as decomposition production and the formation of glycerol ethers can eventually help to improve biodiesel quality in terms of cold flow and viscosity.

When the lard is used as feedstock, the temperature should not be higher than 350 °C according to Shin et al. (Shin et al., 2012). In this case, methyl linoleate (C18:2) accounts for around 11 % out of the total fatty acids in the fat. Above such temperature, the FAME yield is reduced because of the decomposition of the corresponding methyl esters formed. The reaction can be completed at 325 °C after 15 min to obtain a FAME yield of 89.1 %.

Finally, when milder temperatures (below 300 °C) are used, the transesterification reaction requires reaction times up to 60 min. For instance, Manuale et al. (Manuale et al., 2011, 2015) used a temperature of 280 °C to process chicken oil with FAME yields over 90 % after 60 min of operation. Poudel et al. (Poudel et al., 2017) achieved a conversion of 99 % after 60 min at 290 °C using pig fat as feedstock. At lower temperatures, and for the same time, conversion decreased to ~90 % (270 °C) and ~ 75 % (290 °C). The effect of temperature was also studied by Shah et al. (Shah et al., 2015) within the range 220–290 °C using pig fat. Both in ethanol and methanol, the maximum conversion was achieved at the temperature of 290 °C.

As seen, the optimal temperature for the transesterification reaction of animal fats needs to be studied to attain both maximum conversion and FAME yield by minimizing the thermal decomposition of biodiesel. Specifically, polyunsaturated ethyl or methyl esters are more prone to undergo degradation processes in comparison to saturated and mono-unsaturated ones in supercritical conditions (Anitescu & Bruno, 2012).

Pressure effect

Another parameter in supercritical conditions is the pressure of the synthesis mixture to ensure a homogenous reaction media. However, pressure is rarely studied as an independent variable but often measured as an autogenous parameter for a programmed temperature and reaction time. Nevertheless, the reaction pressure can be indirectly adjusted by modifying the amount of solvent (alcohol) and the amount of fat charged in the reactor (Shah et al., 2015). For ethanol and methanol, which are the most frequent solvents in biodiesel production, the operating pressure is usually equal to or higher than 10 MPa to operate in supercritical conditions.

Shin et al. (Shin et al., 2012) specifically studied the effect of pressure on biodiesel synthesis from refined lard. The transesterification reaction was performed with methanol at 335 °C and an alcohol to oil ratio of 45:1 for 20 min under continuous agitation. The pressure was fixed at values of 15, 20, and 25 MPa, respectively, by modifying the amount of alcohol and refined lard loaded in the reactor. An increase in pressure showed a favorable effect on FAME yield to some extent. This effect was more notorious for the first 10 min, but then virtually the same FAME yield was observed for pressures of 20 and 25 MPa. The FAME yield obtained with these pressure values after 20 min (near 90 %) was slightly higher than that achieved with 15 MPa (over 85 %). Additional experiments with waste lard showed that the biodiesel yields were comparable with those offered by refined lard providing a good alternative for biodiesel production.

Often, the reported operating pressures are within the range of 10–20 MPa. Several works employ 10–12 MPa for biodiesel production at different temperatures, reaction times, and fat feedstock such as chicken fat (in methanol at 400 °C and 5–9 min) (Anitescu & Bruno, 2012), chicken oil (in methanol at 280 °C and 60 min) (Manuale et al., 2015), weather tanning waste (in methanol at 335 °C and 10 min) (Ong et al., 2013) and pig fat (in ethanol at 290 °C and 60 min) (Poudel et al., 2017). Values of operating pressured around 20 MPa are also frequent both for short and long reaction times, e.g., conversion of beef tallow (in ethanol at 400 °C and 40 min) (Bolonio et al., 2018).

The main role of pressure implies the tune of the fluid mixture density, proving that it is sufficient to offer good mixing between solvent and reactants and avoiding the formation of multi phases. On the other hand, according to Ong et al. (Ong et al., 2013), once pressure is above the critical point in the synthesis mixture, changes in this parameter are not crucial in terms of kinetic constant rates. Under the equilibrium law by Le Chatelier, a rise in pressure lead to the shift of chemical equilibrium toward the reaction side exhibiting a lower number of moles. As the number of moles is stoichiometrically equal in the two reaction sides of transesterification reactions, it is expected that changes in pressure will not significantly modify chemical equilibrium beyond the supercritical pressure.

Biodiesel quality and properties

The final properties of the product obtained in supercritical conditions directly determine fuel combustion performance. In this sense, biodiesel needs to comply with the specification required in international standards such as ASTM, which establishes limits for present components and physicochemical properties (U.S. Department of Energy, n.d.). In the same way, the European standard EN-14214 requires a minimum value of 96.5 wt% in terms of ester content (European Committee for Standardization, 2003; Marulanda et al., 2010a). Thus, it is necessary to study the features of the biodiesel obtained from animal fats in supercritical conditions to obtain an optimum chemical composition and suitable physicochemical properties.

The chemical composition of the final product can vary depending on the nature of the feedstock used as well as the solvent employed. For example, Poudel et al. (Poudel et al., 2017) found that most of the ester composition in biodiesel obtained from pig fat in supercritical methanol corresponds to methyl heptadecanoate (C17:0), methyl nonadecenoate (C19:1), and methyl nonadecadienoate (C19:2) while the majority components were ethyl stearate (C18:0), ethyl eicosenoate (C20:1) and ethyl eicosadienoate (C20:2) when using supercritical ethanol.

Yuliana et al. (Yuliana et al., 2020) characterized the biodiesel obtained from leather tanning waste in ethanol, comparing the standard specification of biodiesel according to ASTM D6751 (ASTM D6751 - 20a Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, n.d.) and those of conventional diesel fuel

Table 4
Comparison of norm values and reported properties of biodiesel from the works by Yuliana et al. (Yuliana et al., 2020) and Manuale et al. (Manuale et al., 2015).

Properties	Norm method	Norm values	Reported values of biodiesel from animal fat	Anima fat and reference
FAME or FAEE content (wt%)	EN14103	>96.5	97.0 (FAME)	Chicken oil
			97.5 (FAEE)	Leather tanning
Density at 15 °C (kg/m^3)	EN ISO 3675	860–900	876	Chicken oil
			857	Leather tanning
Viscosity at 40 °C (mm^2/s)	ASTM D445	1.9–6	5.7	Chicken oil
			2.37	Leather tanning
Flash point (°C)	ASTM D93	>130	163	Chicken oil
Sulfated ash, (wt%)	ASTM D874	<0.02	0.015	Chicken oil
Conradson carbon (wt%)	ASTM D4530	<0.05	0.02	Chicken oil
Water content (mg/kg)	ASTM D2709	<500	800	Chicken oil
Free fatty acid content (%)	ASTM D664	<0.4	2.7	Chicken oil
Iodine value	EN 14111	<120	100	Chicken oil
Methanol content (wt%)	EN 14110	<0.2	0.15	Chicken oil
Free glycerol (wt%)	ASTM D6584	<0.02	0.019	Chicken oil
Total glycerol (wt%)	ASTM D6584	<0.24	0.17	Chicken oil
Cetane number	ASTM D613	>47	51.2	Leather tanning
Acid number (mg KOH/g)	ASTM D664	<0.05	0.31	Leather tanning
Cloud point (°C)	ASTM D2500	Location and season dependent	9.8	Leather tanning
Calorific value (MJ/kg)	ASTM D240	–	43.451	Leather tanning

under the standard ASTM D975-08 (ASTM D975-08 Standard Specification for Diesel Fuel Oils, n.d.). In terms of viscosity, with a value of 2.36 mm^2 s^{-1}, it was comparable with the specification for conventional diesel. Thus, the biodiesel product can be utilized as a diesel fuel blend without further physical modification. Cetane number and flashpoint of biodiesel were over 51 and 98 °C, respectively, both slightly greater in comparison to the minimum values specified by the ASTM D6751 standard and, therefore, showing satisfactory fuel ignition capacity. The high calorific value was about 43.45 MJ·kg^{-1} and was also within the characteristic range of diesel (42–46 MJ·kg^{-1}). The rest of the final properties were also suitable for fuel performance. For example, the cloud point (measured at 9.8 °C) showed adequate flowability, and the acid value and density were within the ranges established in the ASTM-D6751 standard. This study demonstrates that biodiesel from waste fats is a potential replacement for diesel fuel.

Regarding water content, the standards ASTM-6751 and EN-14214 fix an upper limit of 0.05 % in biodiesel. Biodiesel from chicken oil synthesized in methanol at relatively mild temperatures such as 280 °C, Manuale et al. (Manuale et al., 2011) observed that this requirement could be only attained for reaction times longer than 60 min. At shorter reaction times, the supercritical reaction could not allow synthesized biodiesel to be directly commercialized and thus it should be subjected to a post-treatment stage to remove water e.g., via distillation or flash drum. Manuale et al. (Manuale et al., 2015) also reported that most of the physicochemical properties of the biodiesel obtained from raw chicken oil were in accordance with the norm values. Only the water amount slightly exceeded the established value, and the free fatty acid content was higher than the norm limit. For the sake of clarity, and to facilitate a comparison between norm values and experimental ones for biodiesel obtained from animal fats, Table 4 summarizes the data reported by the works of Yuliana et al. (Yuliana et al., 2020) and Manuale et al. (Manuale et al., 2015), who offered comprehensive information on biodiesel characterization.

The amount of free glycerol is also limited by 0.020 wt% according to the standard ASTMD-6584. Marulanda et al. (Marulanda et al., 2010a) showed that the percentage of free glycerol remained below this value in the biodiesel samples obtained from chicken fat for temperatures from 350 °C and 400 °C in ethanol. Moreover, these authors detected the presence of glycerol ethers in biodiesel, which could be the result of the etherification reactions of glycerol, increasing the valuable components in the fuel (Marulanda-Buitrago & Marulanda-Cardona, 2015).

Anitescu et al. (Anitescu & Bruno, 2012) analyzed the volatility of biodiesel from the transesterification of chicken-derived fat through the advanced distillation curve method. As commented above, when high temperatures are employed (~400 °C), polyunsaturated FAMEs undergo decomposition and convert into lower molecular ester compounds (from C6 to C15 chains) and into hydrocarbons (from C10 to C17 chains). Although this leads to a reduction of FAME yield, the appearance of these lighter-weight components can shift the first portion of the distillation curve toward that of #2 diesel fuel, implying that the overall volatility of supercritical biodiesel is improved when compared to catalysis-based conventional biodiesel product. Moreover, ignition delay can be increased as well as the result of a higher cetane number, enhancing the efficiency of fuel performance.

These results show that the main features of biodiesel established by standards can be generally achieved using animal fats as feedstock.

Techno-economic aspects and environmental impact

A typical flowsheet process for biodiesel production from animal fats would include the following general sections: i) raw material conditioning, ii) reaction unit, iii) product purification and iv) by-product (glycerol) recovery (Kazi & Kazi, 2013). In some cases, the process can be simplified when by-product recovery is not required. Several authors have reported possible process designs for the industrial implementation of supercritical synthesis of biodiesel from animal fats (Manuale et al., 2011, 2015; Marulanda et al., 2010a). As the first step, the feedstock could be pre-treated e.g., by filtration or drying, if necessary, before being loaded into the reactors, which can operate in batch or continuous mode. Since the supercritical process is energetically intensive in terms of temperature and pressure reaction, the recovery of heat is a key factor in significantly reducing the duty heat needed in the process, which is one of the most important cost factors in supercritical technology. In this case, heat exchangers and flash drums have been regarded as suitable equipment for this end. Another important point is the separation and purification of the final product (biodiesel). Methanol or ethanol separation can be accomplished in evaporation units. The resulting biodiesel can be purified through different methods. Manuale et al. (Manuale et al., 2011) have proposed the purification of resulting biodiesel using silica material. Compounds such as mono- and di-glycerides can be conveniently adsorbed on silica beds as well as glycerol and FFA. For cost and resource savings, the alcohol excess could also be recycled into the reaction units. In such a case, the alcohol could be purified in distillation units or dehydrated over solid beds (e.g., zeolites) before recirculation. Manuale et al. (Manuale et al., 2015) have also demonstrated that the generation of glycerol can be virtually avoided when biodiesel is synthesized in supercritical conditions using a moderate excess of alcohol. The content of glycerol present in

the final mixture is even below the limits fixed by quality standards. This implies that glycerol recovery equipment can be avoided with cost savings. The low amount of glycerol in supercritical conditions can be justified by its degradation into low molecular-weight compounds.

In contrast, with the conventional alkali technique, 10%w/w of glycerol is usually attained and its separation from a complex reaction medium (remaining unreacted fats, solvent, soap, catalyst) becomes economically unattractive (Marulanda et al., 2010a). Thus, the disposal of the large amounts of glycerol obtained in conventional synthesis poses an environmental problem (Quispe et al., 2013) that can be overcome using supercritical technology. Therefore, post-treatment stages such as biodiesel washing steps are suppressed, and thus the generation of wastewater effluents.

The optimization of process parameters and heat recovery is crucial to reduce energy consumption. In this respect, very high solvent to oil molar ratios (higher than 40:1) can pose an environmental impact due to the large energy required for the pre-heating and recovery of the alcohol used, and therefore this parameter needs to be carefully analyzed to maintain low solvent/oil ratios. Manuale et al. (Manuale et al., 2015) reported an energy-intensified biodiesel production process in which the enthalpy content of streams coming from the reactor unit is employed for the elimination of the unreacted solvent (methanol) using adiabatic flash drums. A resulting average power duty of 262 W per kg/h of the final product was obtained, which is among the lowest energy consumption reported for supercritical biodiesel synthesis. This corresponds to the total energy consumption of 288 kW for a biodiesel production rate of 1100 kg/h. Most of this energy (92.6 %) is consumed in heater equipment to reach the temperature reaction of 280 °C (267.22 kW) followed by a reboiler column used for the separation of remaining methanol and other volatile compounds from the final biodiesel phase (11.54 kW). Other energy requirements are needed for triglycerides and methanol pumping (5.38 and 4.39 kW, respectively) and biodiesel pumping (0.02 kW). The total energy consumption is also lower than those reported for the subcritical production of biodiesel. While a specific energy consumption of 0.262 kW·h/kg is reported by Manuale et al. (Manuale et al., 2015), the consumption for alkali-based transesterification reaction in subcritical conditions can vary from 0.507 kW·h/kg to 1.136 kW·h/kg (Marulanda et al., 2010b).

According to the above information, supercritical synthesis of biodiesel from animal fats is regarded as a simpler, cost-effective, and less expensive method when compared to conventional catalysis-based processes such as alkali transesterification. This last option includes a higher number of stages, and the involvement of a catalyst leads to the use of larger effluent volumes to be disposed of or/and treated.

Although methanol is extensively used as a low-cost solvent in supercritical processes, it poses some risks such as environmental toxicity. On its part, ethanol can be obtained from renewable sources, and it is safer to handle. Due to these properties, ethanol is regarded as the most suitable alcohol option for biodiesel production via supercritical technology (Sakdasri et al., 2017).

Animal fats are an interesting feedstock for biodiesel production as they present a lower cost in comparison to vegetable oils partly because the market for animal fats is more limited. They are considered waste materials in many markets (e.g., in USA) and thus they can be valorization into biofuels, which promotes a green economy (Khan et al., 2021). Moreover, the biodiesel obtained from animal fats has proven to produce a smaller increase or no increase in NOx emission in comparison to vegetable oil-derived biodiesel probably due to a higher cetane number (higher than 60 versus 48–55 for vegetable oil biodiesel). A higher cetane number implies lower NOx emissions by the reduction of the temperature during the early stage of combustion (Tat et al., 2007).

Finally, valorizing residual animal fats with low commercial value as feedstock in the production of biodiesel can contribute to mitigating climate change by reducing GHGs emissions associated with fossil fuels, since biodiesel will partially or totally substitute diesel in transport vehicles. In this sense, the use of waste animal fats as a new source of biodiesel is aligned to the Directive 2012/1513 of the European Parliament and of the Council which modifies the Directive CE/28/2009, on the promotion of energy from renewable sources that fosters a more sustainable production of fuels. In addition, this type of feedstock will contribute to the goal set by the EU of replacing 10 % of fossil fuels consumed by European vehicles and a 20 % reduction in emissions of greenhouse gases (SEC (2011) 130 final). In addition, this is also aligned with the European Directive for the Efficient Use of Resources 2020, whose main objective is to support the transition to an economy in which natural resources are properly used to achieve sustainable growth with lower carbon emissions.

Conclusions

Waste animal fats have attracted growing research attention as biodiesel feedstock in the last years. Moreover, supercritical transesterification is regarded as a suitable technology with advantages over subcritical catalytic conversion especially in terms of reaction time, solvent (alcohol) excess, and tolerance toward the presence of impurities in the feedstock. The PRISMA approach has been applied to conduct this systematic review, analyzing key articles on the synthesis of biodiesel from animal fats in supercritical media and highlighting the drawbacks and advantages of the reported production strategies. The effects of fundamental factors, e.g., lipid composition, operating conditions such as reaction time, temperature, pressure, solvent amount, and water content have been discussed. A broad variety of animal and waste fats have been used as feedstocks for biodiesel production, e.g., chicken fat, chicken oil, refined lard, leather tanning waste, beef tallow, or pig fat, among others. Animal fats can present higher free fatty acid and water contents compared to vegetable oils. Even though, their use as biodiesel feedstock is considered suitable and advantageous due to its low cost. Temperature and reaction time are especially significant since these parameters need to be balanced to achieve high FAME/FAEE yields and simultaneously prevent the thermal decomposition of the final product. In this sense, feedstocks with a low amount of polyunsaturated fatty acids are desirable since they are more prone to undergo decomposition processes. As seen, ethanol and methanol are among the most common solvents, and specifically, methanol is the most frequently used because the FAMEs extraction from the reaction media is easier compared with the extraction of FAEEs. The final properties of the product obtained in supercritical conditions directly determine fuel combustion performance and the products obtained from waste animal fats can meet the specifications posed by international standards. In addition, the production of biodiesel from animal fats is considered a simple and cost-effective method when compared to conventional catalysis-based synthesis such as alkali transesterification, enabling the valorization of wastes such as non-edible animal fats. Thus, waste fats are promising candidates to produce biodiesel. Future works may delve into the intensification process in continuous mode and the upscaling of the technology for industrial implementation. Moreover, further articles should report the sample mean and standard deviation of parameters such as the FAME or FAEE yields to perform a meta-analysis in the near future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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